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(54) COLOURED LUSTROUS PIGMENTS

(71) We, MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 250, Frankfurter Strasse, 61 Darmstadt, Federal Republic of Germany, a Joint-Stock Company organised under the laws of the Federal Republic of Germany,

do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new coloured lustrous pigments.

Coloured lustrous pigments are of increasing interest in various fields, for example, in cosmetics and as additives for synthetic resins, lacquers and dyes. Due to the ever increasing possibilities of use, there is a need for new colour shades.

It is already known to add dyestuffs to lustrous pigments during the production thereof so that, in addition to the colours due to interference phenomena, additional colour effects can be achieved. Thus, for example, according to German Patent Specification No. 2,124,155, dyestuffs are added during the formation of lustrous pigments based on triazines, uracils and basic lead carbonate, the dyestuffs being incorporated into the pigment particles. Furthermore it is known, for example, from German Patent Specification No. 1,192,353, to achieve a better adhesion of the dyestuffs to the pigment particles by producing water-insoluble dyestuffs directly in a suspension which contains the pigment particles, the dyestuff thereby being deposited in finely-divided form directly upon the pigment particles.

However, these processes do not satisfy the practical requirements. It has been shown that, in this way, only a part of the dyestuff is fixed on to the pigment particles. The greater part of the dyestuff does not precipitate out on the pigment particles but is present in suspension. The dyestuff can also be easily washed off from the pigments with water. Furthermore, in most cases, a non-uniform distribution of the dyestuff on the pigment surface is observed, which considerably impairs the properties of the end products, especially their gloss.

It is an object of the present invention to provide improved coloured lustrous pigments with special colour effects in a technically simple manner, this object being achieved when the dyestuff is chemically and not only adsorptively bound to the surface of the pigment particles. This is possible by providing the starting material with a coating which can be converted into a coloured lake. Coloured lustrous pigments are thereby obtained with a firmly adhering dyestuff coating which cannot be washed out and the pigments obtained have an outstanding colour and luminous power and, in addition, display metallic gloss colour effects which cannot be achieved with the previously known lustrous pigments.

Thus, according to the present invention, there is provided a coloured lustrous pigment based on mica flakes coated on both sides with an adherent coating of a metal oxide, wherein colouring is provided by an aluminium colour lake fixed, with the help of an aluminium hydroxide layer which has previously been precipitated on the metal oxide-coated mica flakes, as a water-insoluble compound on the surface of the pigment particles.

The pigments preferably contain the aluminium colour lake in an amount of 0.001 to 5% by weight, referred to the total coloured pigment.

The present invention also provides a process for the production of coloured lustrous pigments based on mica flakes coated on both sides with an adherent coating of a metal oxide, wherein a lustrous metal oxide-coated mica flake pigment with an aluminium hydroxide layer precipitated thereon is reacted with an aqueous solution of a hydroxyl group-containing compound which, directly or with the intermediate formation of a sparingly water-soluble precipitate with aluminium ions and subsequent reaction thereof with a diazotised amine, forms a water-insoluble aluminium colour lake.

The hydroxyl group-containing compound used is preferably either an organic dyestuff

which forms a sparingly water-soluble simple or complex salt with aluminium ions or is a chelate former which forms, with aluminium ions, a sparingly water-soluble precipitate, this precipitate being subsequently converted by a conventional coupling reaction with a diazotised amine, into a water-insoluble aluminium colour lake.

The new pigments according to the present invention can be produced from all known pigments based on mica flakes coated on both sides with an adherent uniform coating of a metal oxide. Such pigments are commercially available and are described, for example, in German Patent Specification No. 2,009,566. As a rule, such mica flakes have a diameter of about 5—200 microns and a thickness of between 1 and 5 microns and preferably of about 0.5 micron. As metal oxide coatings, there are mainly used, because of the advantageous refractive index, titanium dioxide or titanium dioxide aquate and/or zirconium dioxide or zirconium dioxide aquate. An especially frequently used pigment is, for example, a mica flake pigment in which mica flakes with a diameter of 5 to 50 microns and a thickness of about 0.5 micron are uniformly coated with an optionally hydrated titanium dioxide layer, the mica surface containing 50 to 500 mg. TiO_2/m^2. These known lustrous pigments have various colours, depending upon the layer thickness of the precipitated titanium dioxide and/or zirconium dioxide layer. As a rule, the products are calcined. In principle, however, there can, of course, be used all other pigments based on metal oxide-coated mica flakes and especially those with other layer thicknesses of titanium dioxide and/or zirconium dioxide. Furthermore, as starting materials, there can be used all lustrous pigments which contain coloured metal oxides in the layers present on the mica flakes, for example, oxides of iron, nickel, cobalt, chromium or vanadium. These layers can, if desired, also contain non-coloured metal oxides, such as aluminium oxide or antimony oxide. These pigments are also known and are described, for example, in German Patent Specifications Nos. 1,467,468; 1,959,998 and 2,244,298.

A coating of aluminium hydroxide is first applied to these pigments which forms a firmly adhering layer and makes the pigment particles colourable. The aluminium ions contained therein can then be reacted to form a firmly adhering coloured layer.

The coating with aluminium hydroxide of lustrous pigments based on mica flakes coated with metal oxides is known. For the carrying out of this coating, the pigment particles are suspended in water and the suspension is expediently heated to a temperature of, for example, between 40 and 95°C. An aqueous acidic solution of a water-soluble aluminium salt, for example, of aluminium chloride, aluminium nitrate, potassium aluminium sulphate or aluminium sulphate, or an aqueous alkaline solution of an aluminate, for example, of sodium aluminate or potassium aluminate, is then allowed to flow into the suspension. The concentration of aluminium ions in the added salt solution is preferably between 0.1 and 5 mol/litre.

Simultaneously, an alkali or acid is added thereto in order to adjust the pH to a value between 3 and 10 and preferably between 4 and 9. The alkali used is preferably an alkali metal or ammonium hydroxide and more preferably either an aqueous solution of sodium hydroxide or gaseous ammonia. In the case of adding an acid, it is preferred to use hydrochloric, sulphuric or nitric acid.

The addition of alkali or acid is so regulated that the pH value of the suspension remains as constant as possible during the precipitation. After the precipitation of the desired amount of aluminium hydroxide, the pigment obtained is filtered off with suction, washed and dried. It has proved to be advantageous to adjust the precipitated amount of aluminium hydroxide to 0.1 to 20% by weight (as aluminium oxide) in the finished pigment and preferably to 1 to 10% by weight. This corresponds to a thickness of the aluminium hydroxide layer of 1 to 100 nm.

An isolation and drying of the so coated pigment is, in many cases, not necessary. On the contrary, the suspension of the coated pigment particles obtained from the aluminium hydroxide precipitation step can be used directly in the following step, in which the colour lake is produced.

The aluminium hydroxide layer so obtained on the pigment particles is smooth and uniform so that the gloss and colour power of the coloured pigments obtained can be fully displayed. In contradistinction to a direct coating with organic dyestuffs, in the case of coating with aluminium hydroxide, the appearance of co-precipitations and the formation of dyestuff agglomerates are avoided.

This base layer of aluminium hydroxide enables the pigment particles to be coloured in a further step, the sole requirement for the substance to be used being that it must be able to form a lake with aluminium ions. As is known, according to definition, colour lakes are obtained by the precipitation of a water-soluble organic dyestuff with a precipitation agent and especially with metal ions, i.e. in the present case, aluminium ions. Thus, an appropriate selection can be made from the numerous available dyestuffs. Numerous aluminium colour lakes are described in the literature. Furthermore, many organic compounds are known which can form colour lakes with aluminium so that the process according to the present invention and the new pigments are not limited to the known aluminium colour lakes. Therefore, the pro-

cess according to the present invention is readily applicable to a plurality of dyestuffs, a broad field of application also being given amongst the foodstuff dyestuffs and the cosmetic colours.

The formation of the colour lake on the pigment particles coated with aluminium hydroxide can take place in various known ways. The inorganic components of the colour lake composed of an organic and an inorganic component are the aluminium ions which are firmly fixed on to the pigment particles in the form of a smooth and firmly adhering aluminium hydroxide layer. The organic component, which is needed for the formation of the colour lake, is a dyestuff molecule which contains groups which permit either the formation of a sparingly water-soluble salt or of a sparingly water-soluble complex compound with aluminium ions. According to the present invention, those molecules are preferred which are able to form true complex compounds with aluminium ions because such compounds generally permit the expectation of a greater chemical stability than do simple salts. Materials of this type which can be used for complex formation are, for example, already much used in analysis as metal indicators or as precipitation reagents. They are also known in dyeing technology *inter alia* as mordant dyestuffs. In other words, a large variety of colour lakes can be used. Dyestuffs with chelate-forming groups, for example dyestuffs based on anthraquinone and especially the alizarin complex compounds known for the production of madder lakes, are especially advantageous. In dyestuffs with salt-forming groups, the number of salt-forming groups must, on the one hand, be so great that the dyestuff can initially be kept in aqueous solution but, on the other hand, also so small that, after the reaction with the pigment particles, a sparingly water-soluble salt is formed which cannot be washed out. Consequently, the number of the salt-forming groups plays a part in the relationship to the size and form of the organic molecule. In principle, these reactions are well known but, in case of doubt, a routine experiment suffices to ascertain whether a particular dyestuff forms a sparingly water-soluble colour lake with aluminium ions.

The formation of the colour lake can take place in two ways:

Method A

Pigment particles coated with aluminium hydroxide are slurried in water. A solution of the selected organic dyestuff is slowly added thereto and the suspension is heated. The dyestuff thereby reacts with the aluminium hydroxide on the pigment particles with the formation of a colour lake, so that the pigment particles become coloured. For the colour depth, the concentration of the dyestuff solution is especially decisive but the pH value of the suspension and the reaction temperature also exert an influence.

Method B

Pigment particles coated with aluminium hydroxide are reacted in aqueous suspension with an organic compound which is able to form a sparingly water-soluble precipitate with aluminium ions.

These organic compounds are preferably chelate formers, for example hydroxyquinolines. The layer of a sparingly water-soluble aluminium chelate formed in this manner now permits, by coupling with, for example, diazotised amines of the most varied type, dyestuffs to be fixed on to the pigment particles. For this purpose, the diazotised amines are dosed into the aqueous pigment suspension. The dyestuff forming in known manner by coupling is firmly fixed on to the pigment particles and forms a dyestuff layer which cannot be washed out.

This process opens up a large variety of possibilities for the formation of the colour lakes since, as is known from the appropriate literature, the number of dyestuffs producable *via* diazotisation and coupling is almost unlimited. The layer adhering to the pigment particles and bound with the aluminium ions to a firm chelate complex is thus the starting point for a plurality of coloured pigments.

In the case of Method A, the concentration of the dyestuff solutions which are supplied to the pigment particles coated with aluminium hydroxide and present in suspension can be approximately between 0.001 and 5% by weight and is preferably between 1 and 3% by weight.

These ranges are not critical since, depending upon the desired colour depth, different amounts of dyestuffs can, of course, be added thereto. The amount of dyestuff fixed on to the pigment particles with the help of the aluminium hydroxide layer depends upon the molecular weight of the dyestuff in question. However, in general, it is between 0.001 and 5%, referred to the coloured pigment.

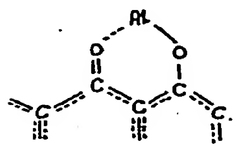
The individual dyestuffs mentioned in the following are not a complete enumeration of all possible chelate-forming configurations. The mechanism of the process according to the present invention is merely to be made clear on the basis of these examples and it is not to represent a limitation with regard to other dyestuffs not specifically mentioned. It will be readily appreciated which other dyestuffs can be employed in carrying out the process according to the present invention. The division of the dyestuffs into individual groups is also not to be regarded as being a limitation. Furthermore, it is obvious that a particular dyestuff can also belong simultaneously to several groups, for example, when, in addition

to chelate-forming parts, salt-forming parts are also present in the molecule.

1. Dyestuffs with chelate-forming groups

1.1 Dyestuffs based on anthraquinone

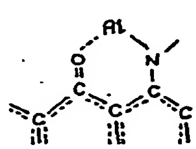
1.1.1 OH groups neighbouring a CO group. The decisive grouping in the molecule for the complex formation is the following:—



These include the alizarin complex compounds known for the production of the madder lakes, which are especially preferred. By way of example, there may be mentioned:

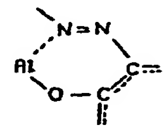
1,2-dihydroxyanthraquinone - 3 - sulphonic acid (Alizarin S)
1,2,5,8 - tetrahydroanthraquinone carminic acid
1,2,6 - trihydroxyanthraquinone - 3-sulphonic acid
1,4 - dihydroxy - anthraquinone - 2-sulphonic acid
1,2-dihydroxyanthraquinone
1,2,3 - trihydroxyanthraquinone
1,2,4-trihydroxyanthraquinone
1,2,5-trihydroxyanthraquinone
1,2,6-trihydroxyanthraquinone
1,2,7-trihydroxyanthraquinone
1,2,4,5,8-pentahydroxyanthraquinone
1,2,4,5,7,8-hexahydroxyanthraquinone
3 - nitro - 1,2 - dihydroxyanthraquinone
4-amino-1,2-dihydroxyanthraquinone
3 - amino - 1,2,4 - trihydroxyanthraquinone
4-nitro-1,2-dihydroxyanthraquinone
1-salicylaminoanthraquinone
dibenzoyl-1,5-diaminoanthraquinone
dibenzoyl-1,8-diaminoanthraquinone
[(1,4 - dihydroxy - 2 - anthraquinonyl)-methyl] - imino - diacetic acid
[(3,4 - dihydroxy - 2 - anthraquinonyl)-methyl] - imino - diacetic acid (alizarin complexan)

1.1.2 Amino groups neighbouring a CO group. The complex formation takes place as follows:—



To these belong, for example:
1,4 - di - (4′ - methyl - 2′ - sulphophenylamino) - anthraquinone

1.2 Azo compounds with neighbouring hydroxyl groups. Complex formation can take place between a diazo group and a neighbouring hydroxyl group:



The following monoazo dyestuffs can, for example, be used:

1 - (2 - sulpho - 4 - methyl - 1 - phenylazo) - 2 - naphthol - 3 - carboxylic acid (Litholrubin BK)
1 - (2 - sulpho - 4 - methyl - 5 - chloro-1 - phenylazo) - 2 - hydroxynaphthalene - 3 - carboxylic acid (Litholrubin 3R)
1 - (3 - sulpho - 1 - phenylazo) - 2-naphthol - 6 - sulphonic acid (Orange GGN)
1 - (2 - sulphonic acid - 4 - chloro - 5-carboxylic acid - 1 - phenylazo) - 2-hydroxynaphthalene (permanent red toner NCR)
1 - (4 - sulpho - 1 - phenylazo) - 2-naphthol - 6 - sulphonic acid (yellow-orange S)
4 - (4 - sulpho - 1 - phenylazo) - 1 - (4-sulphophenyl) - 5 - hydroxypyrazolone - 3 - carboxylic acid (tartrazine)
2,4 - dihydroxy - azobenzene - 4′ - sulphonic acid (chrysoin S)
1 - (2 - sulpho - 1 - naphthylazo) - 2-hydroxynaphthalene - 3 - carboxylic acid (Lithol bordeaux toner R)
1 - (4 - sulpho - 1 - naphthylazo) - 2-naphthol - 3,6 - disulphonic acid (amaranth)
2 - (4 - sulpho - 1 - naphthylazo) - 1-naphthol - 4 - sulphonic acid (azombin)
1 - (4 - sulpho - 1 - naphthylazo) - 2-naphthol - 6,8 - disulphonic acid (cochineal red A)
1 - (6 - hydroxy - *m* - toloylazo) - 2-naphthol - 4 - sulphonic acid (calmagite)
bis - [3 - (8 - amino - 1 - hydroxy - 3,6-disulpho - 2 - naphthylazo) - 4 - hydroxyphenyl] - sulphone (sulphonazo)
3 - hydroxy - 4 - (2 - hydroxy - 4 - sulpho - 1 - naphthylazo) - 2 - naphthoic acid (calcone carboxylic acid)
4 - (2 - pyridylazo) - resorcinol (PAR)
1 - (2 - hydroxy - 1 - naphthylazo) - 2-naphthol - 4 - sulphonic acid (calcone)

3 - (5 - chloro - 2 - hydroxyphenylazo)-4,5 - dihydroxy - 2,7 - naphthalene-disulphonic acid (eriochrome blue SB)

1 - (2,4 - dimethyl - 1 - phenylazo) - 3,6-disulpho - 2 - naphthol (Ponceau R)

1 - (1 - hydroxy - 2 - naphthylazo) - 6-nitro - 2 - naphthol - 4 - sulphonic acid (Erio T)

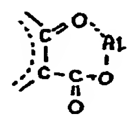
The following diazo dyestuffs can, for example, also be used:

[4' - (4" - sulpho - 1" - phenylazo) - 7'-sulpho - 1' - naphthylazo] - 1 - hydroxy - 8 - acetylaminonaphthalene-3,5 - disulphonic acid (brilliant black BN)

2 - [4' - (4" - sulpho - 1" - phenylazo)-7' - sulpho - 1' - naphthylazo] - 1-hydroxy - 7 - aminonaphthalene - 3,6-disulphonic acid (Black 7984)

1.3 Dyestuffs with neighbouring COOH and CO groups.

Here again, complex formation takes place with the aluminium ion:



By way of example, there are mentioned:

5 - (3,3' - dicarboxy - 4,4' - dihydroxy-benzohydrylidene) - 2 - oxo - cyclohexa - 3,6 - diene - 1 - carboxylic acid (aurin tricarboxylic acid)

5 - [α - (3 - carboxy - 5 - methyl - 4-oxo - cyclohexa - 2,5 - dien - 1-ylidene) - 2,6 - dichloro - 3 - sulphobenzyl] - 3 - methylsalicylic acid (Chromazurol S)

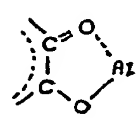
5 - [α - (3 - carboxy - 5 - methyl - 4-oxo - cyclohexa - 2,5 - dien - 1 - ylidene) - 2,6 - dichlorobenzyl] - 3-methyl - salicylic acid (eriochromazurol B)

5 - [α - (3 - carboxy - 5 - methyl - 4-oxo - cyclohexa - 2,5 - dien - 1 - ylidene) - 2 - sulphobenzyl] - 3 - methyl-salicylic acid (eriochromcyanin R)

5 - [3 - carboxy - α - (3 - carboxy - 5-methyl - 4 - oxo - cyclohexa - 2,5-dien - 1 - ylidene) - 4 - hydroxy - 2,6-dimethyl - benzyl] - 3 - methyl - salicylic acid (chromoxan violet 5B)

1.4 Dyestuffs with neighbouring OH and CO groups.

Complex formation takes place as follows:



Examples of such dyestuffs include the following:

pyrocatechol sulphonphthalein (pyrocatechol violet)

o - (4,5,6 - trihydroxy - 3 - oxo - 3 - H-xanthen - 9 - yl) - benzene - sulphonic acid (pyrogallol red)

o - (2,7 - dibromo - 4,5,6 - trihydroxy - 3-oxo - 3 - H - xanthen - 9 - yl) - benzene - sulphonic acid (bromopyrogallol red)

o - (2,6,7 - trihydroxy - 3 - oxo - 3 - H-xonthen - 9 - yl) - benzene - sulphonic acid (hydroxyhydroquinone pink)

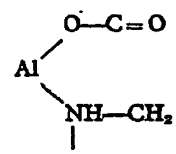
4',5' - dihydroxyfluorescein (gallein)

2',7' - tetrahydroxyfluorescein (hydroxyhydroquinone - phthalein)

3' - hydroxyphenylphthalein (pyrocatechol blue)

1.5 Dyestuffs with an aminoacetic acid grouping.

Complex formation takes place in the following manner:



The following dyestuffs are mentioned by way of example:

2',7' - bis - {[bis - (carboxymethyl)-amino] - methyl} - fluorescein (calcein)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - diisopropyl-2',2" - dimethylphenolsulphonphthalein (methyl thymol blue)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - dimethyl-phenolsulphonphthalein (xylenol orange)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - dimethyl-phenolsulphonphthalein (glycine cresol red)

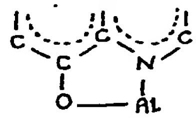
3',3" - bis - {[bis - (carboxymethyl)-omino] - methyl} - phenolphthalein (phenolphthalexone)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - dimethyl-phenolphthalein (cresolphthalexone)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - diisopropyl-2',2" - dimethylphenolsulphonphthalein (glycine thymol blue)

3',3" - bis - {[bis - (carboxymethyl)-amino] - methyl} - 5',5" - diisopropyl-2',2" - dimethylphenolphthalein (thymolphthalexone)

1.6 Dyestuffs with the grouping:



By way of example, there is mentioned:

α - (8 - hydroxy - 5 - quinolyl) - α - (4-oxo - cyclohexa - 2,5 - dien - 1 - ylidene) - *o* - toloylic acid (oxine blue)

2. Dyestuffs with salt-forming groups (without chelate formation).

N,N - diphenylrosaniline - monosulphonic acid } (alkali blue)
N,N - triphenylrosaniline - monosulphonic acid }

quinophthalone - disulphonic acid (quinoline yellow)

indigo - disulphonic acid

2,4 - disulpho - 5 - hydroxy - 4,4′ - bis-(diethylamino) - triphenyl - carbinol (Patent Blue V)

N,N′ - diethyl - N,N′ - disulphobenzyl-di - 4 - amino - 2 - chloro - di - 2-methyl - fuchsonimonium (Acilanechtgrun 10 G)

4′ - (N - ethyl - N - *m* - sulphobenzyl-amino) - 4″ - (N - dimethylamino) - N-ethyl - N - *m* - sulphobenzyl - fuchsonimonium tetrabromo - dichlorofluorescein (phloxin)

2,4,5,7 - tetraiodofluorescein (erythrosin bluish).

For the formation of the aluminium colour lakes, there can also be used the so-called eloxal dyes, which are available for colouring eloxalated aluminium. As a rule, these are coloured, organic metal complexes and especially chromium or copper complexes. They are usually dyestuffs which are characterised by an especially good stability and light fastness. By way of example, there are mentioned the chromium complexes of Zaponechtgelb G [N - (*o* - hydroxybenzylidene) - 2 - hydroxy-3 - sulpho - 5 - nitrophenylamine], Palatinechtorange GN [4 - (3′ - nitro - 5′-sulpho - 6′ - hydroxy - 1′ - phenylazo) - 1-phenyl - 3 - methyl - 5 - hydroxypyrazole], Palatinechtrot BEN, Palatinechtschwarz WAN [2 - (2 - hydroxy - 4 - sulpho - 6 - nitro - 1-naphthylazo) - 2 - naphthol] and, for example, Heliogenblau SBL [copper phthalocyanine - sulphonic acid].

The aluminium chelate precipitate to be formed according to Method B is also produced from solutions which are added to the pigment particles coated with aluminium hydroxide and present in suspension. Examples of chelate formers include 2,4- and 2,6-dihydroxybenzoic acid, 8 - hydroxyquinoline and gallic acid. However, other compounds can also be employed which form, with aluminium ions, chelates which are sparingly soluble in water. For carrying out the process, the pigment coated with aluminium hydroxide is mixed with a solution of the complex former and boiled or at least brought to an elevated temperature (>30°C.) at a pH value appropriate for the complex formation, which is normally between 3 and 10, for some time, for example, 5 to 30 minutes.

The addition of a conventional buffer solution, for example of an acetate or glycocol buffer, is frequently recommendable. The so treated pigment is filtered off and washed with water or also with buffer solution and subsequently with water. In some cases, it is also desirable to add the complex formers in alcoholic solution; in this case, it is also preferable to wash with an aqueous alcoholic solution or with an alcohol. The so-obtained pigment is then reacted in aqueous suspension with a diazotised amine. The reaction is normally carried out at ambient temperature and in a substantially neutral medium. In principal, the usual standard processes for coupling reactions for the production of azo dyestuffs can be used.

In principle, all amines suitable for the formation of azo dyestuffs can be employed. Primary aromatic amines are preferred, especially those with additionally contain sulphonic and/or carboxylic acid groups. From the vast number of these compounds, there may be mentioned, by way of example:—

aniline
naphthylamine
2-aminobenzoic acid
sulphanilic acid
4-aminonaphthalene-1-sulphonic acid
4-amino-2-hydroxybenzoic acid
4 - amino - 5 - hydroxy - naphthalene - 2,7-disulphonic acid
4 - amino - 3 - hydroxynaphthalene - 1 - sulphonic acid
6 - amino - 5 - hydroxynaphthalene - 1 - sulphonic acid
1-amino-4-hydroxyanthraquinone.

The coloured pigment particles can be separated from the suspension, repeatedly washed with water, possibly also with an alcohol and then dried, preferably at temperatures of about 120°C. at atmospheric pressure or at correspondingly lower temperatures when using a reduced pressure.

When colouring the pigments containing a base layer of aluminium hydroxide with a selected dyestuff, no agglomeration takes place since no further precipitation occurs which could bring about adhesion of the pigment particles. Therefore, the process according to the present invention always gives strongly-coloured, good glossy pigments. The new process is thus also far superior to the known methods. Precisely the pigments based on mica flakes and coated with metal oxides tend very frequently to agglomerate, especially when organic dyestuffs are precipitated out in

the presence thereof. The gloss and colour power thereby decrease considerably and the agglomerated particles are coated with dyestuff and thus stick together. Subsequent separation thereof is not possible. Therefore, colouring such pigments according to the known processes is only possible to a limited extent.

All the new coloured pigments according to the present invention can be employed in the same way as those previously known, i.e. as additives for synthetic resins, dyestuffs or lacquers but especially for cosmetics. The new lustrous pigments are usually added in amounts of between 0.1 and 80% by weight. Cosmetic compositions include powders, salves and wax pencils, for example, eye lid shadow pencils (pigment content 5 to 15%), eye lid shadow powder compacts (pigment content 20 to 70%), liquid compositions for eye lid shadows and eye lid coating (pigment content 7 to 15%), lipsticks (pigment content 10 to 20%), lip gloss cream for painting on (pigment content 10 to 15%), make-up in pencil form (pigment content 15 to 25%), make-up powder compacts (pigment content 10 to 50%), make-up emulsions (pigment content 5 to 10%), make-up fatty gel (pigment content 1 to 5%), light protection emulsions and tanning emulsions (pigment content 5 to 10%), foam bath concentrates with colour gloss (pigment content 0.1 to 2%) and skin care lotions (pigment content 0.1 to 2%).

An advantage of the pigments according to the present invention when used in cosmetics is that an outstanding colour gloss is produced, such as is desired for many decorative cosmetics. Furthermore, the pigments according to the present invention are characterised by their simple use as master batches since here, in one substance, colour and gloss components are combined, which otherwise would require the separate use of colour and gloss pigments.

The following Examples are given for the purpose of illustrating the present invention:—

Example 1.

a) 6 kg. of a mica flake pigment with silver gloss (platelet size between 10 and 50 μ, titanium dioxide content 28% by weight, mica content 72% by weight) are suspended in completely desalinated water and heated, with stirring, to 75°C. A pH of 8 is obtained by the addition of aqueous sodium hydroxide solution. A solution of 850 g aluminium chloride hexahydrate in 35 litres of water is allowed to run in slowly at a rate of about 35 liters/hour. Simultaneously, a 7.5% by weight aqueous sodium hydroxide solution is so dosed in that the pH value of 8 is kept constant over the whole of the reaction period. Subsequently, the reaction batch is further stirred for an hour. The pigment is then filtered off and washed with completely desalinated water and dried at 120°C. The aluminium oxide content is 2.9% by weight.

b) 5 kg. of the product obtained according to a) above are suspended in 100 litres of an ammonium acetate-acetic acid buffer solution (pH 5). The suspension is heated, while stirring, to about 90°C. and subsequently mixed with a solution of 100 g. 1 - (2 - sulpho - 4-methylphenylazo) - 2 - hydroxy - naphthalene-3 - carboxylic acid (C-red 12) in 100 litres of completely desalinated water. After about 30 minutes, the product is filtered off and washed with water and acetone to remove excess dyestuff. It is then dried at 110°C.

The pigment thus obtained is uniformly coated with an aluminium colour lake and has a pink lustre with a strong red powder colour.

Example 2.

a) 60 g. of a lustrous pigment with blue interference colour (platelet size between 10 and 50 μ, titanium dioxide content 50% by weight, mica content 50% by weight) are suspended in 2 litres of completely desalinated water and heated, while stirring, to 75°C. The pH value is adjusted to 5 by the addition of hydrochloric acid. 350 ml. of a solution, which contains 50 g potassium aluminium sulphate dodecahydrate per litre of completely desalinated water, is allowed to run in at a rate of 350 ml./hour. By the simultaneous dosing in of 2.5% solution of ammonium hydroxide, the pH value is kept constant at 5. The reaction batch is further stirred for about 1 hour, whereafter the pigment is filtered off, washed salt-free with water and dried at 120°C. The pigment obtained possesses a firmly adhering layer of aluminium oxide hydrate, the content of aluminium oxide being 3.1% by weight.

b) 5 g. of the preparation obtained according to Example a) are suspended in 100 ml. of an acetate buffer solution (pH 4.5). The suspension is heated, while stirring, to about 90°C., whereupon a solution of 100 mg. 2-[4' - (4'' - sulpho - 1'' - phenylazo) - 7'-sulpho - 1' - naphthylazo] - 1 - hydroxy - 7-aminonaphthalene - 3,6 - disulphonic acid (C-black 7) in 100 ml. completely desalinated water is added thereto. After about 30 minutes, the product is filtered off, washed with water and acetone to remove excess dyestuff and dried at 120°C.

The pigment so obtained with the colour lake has a deep blue powder colour and a luminescent blue intereference colour. Its colour power is far superior to that of the starting pigment.

Example 3.

60 g. of a mica flake pigment coated with titanium dioxide, with red-blue intereference colour (platelet size between 10 and 50 μ, titanium dioxide content 47% by weight, mica

content 53% by weight) are suspended in 2 litres of completely desalinated water and coated with aluminium hydroxide in the manner described in Example 1a).

5 g. of the dried product are suspended in 100 ml. water and heated, while stirring, to about 90°C., whereupon a solution of 50 mg. 4' - (N - ethyl - N - *m* - sulphobenzyl-amino) - 4'' - (N - dimethyl - amino) - N-ethyl - N - *m* - sulphobenzyl - fuchsonimonium (C-ext-violet 15) in 100 ml. water is added thereto. After about 30 minutes, the coloured pigment is filtered off and washed with water and acetone to remove excess dyestuff. The pigment obtained has a strong violet powder colour and displays a reddish-violet gloss through the colour lake coating.

Example 4.

60 g. of a mica flake pigment, coated with titanium dioxide, with yellow intereference colour (platelet size between 10 and 50 *u*, titanium dioxide content 42% by weight, mica content 58% by weight) are suspended in 2 litres of water and coated with aluminium hydroxide in the manner described in Example 1a). 10 g. of this pigment are suspended in 100 ml. of an acetate buffer solution (pH 4.5). To this suspension is added a solution of 0.01 mol sodium 2,6-dihydroxybenzoate in a little water, whereafter the mixture is heated for 10 minutes to about 90°C. Subsequently, the pigment pre-treated in this manner is filtered off and washed several times with water. The product, which possesses a firmly adhering aluminium chelate layer, is dried at 110°C.

The pigment pre-treated in this manner is again slurried in an acetate buffer solution (pH 4.5) and mixed at ambient temperature with an aqueous solution of 0.01 mol diazotised sulphanilic acid. The formation of the azo dyestuff commences rapidly, a deep yellow coloured pigment being obtained which displays a lively gold gloss.

Example 5.

10 g. of a mica flake pigment of yellow interference colour, coated with aluminium hydroxide in the manner described in Example 1a), are suspended in 100 ml. acetate buffer solution (pH 4). To this suspension is added a solution of 0.005 mol sodium 2,4 - dihydroxybenzoate in a little water. The mixture is heated for 20 minutes to about 85°C., whereafter the product is filtered off and thoroughly washed with water. The pigment can be dried at 110°C.

5 g. of the so obtained product are again slurried in an acteate buffer solution (pH 5) and mixed with 10 ml. (0.005 mol) of an aqueous solution of diazotised 2 - aminobenzoic acid. The immediately commencing formation of the azo dyestuff gives an orange coloured pigment with a red-gold lustre.

Example 6.

10 g. of a titanium dioxide mica flake pigment, coated with aluminium hydroxide in the manner described in Example 1a), with a red interference colour, are suspended in 100 ml. water. To this suspension is added, with stirring, a solution of 0.001 mol 8-hydroxyquinoline in 15 ml. ethanol. The suspension is adjusted to a pH value of 5. The reaction mixture is heated to boiling temperature and kept at this temperature for about 10 minutes. Subsequently, the product is filtered off, washed several times with water and alcohol and dried at 110°C.

5 g. of the so obtained product are again suspended in 50 ml. of an acetate buffer solution (pH 4.6) and mixed at ambient temperature with an aqueous solution of 0.15 g. diazotised aniline. The dyestuff formed adheres firmly to the pigment particles to give a bright yellow colour pigment with a reddish-yellow interference colour.

Example 7.

Analogously to Example 1a), a series of mico-titanium dioxide pigments with various interference colours are coated with aluminium hydroxide. 5 g. amounts of the products so obtained are suspended in 100 ml. of an aqueous acetate buffer (pH 4.7) and mixed, in the manner described in Example 1b), with a solution of 100 mg. of one of the dyestuffs mentioned in the following Table I in 100 ml. completely desalinated water at boiling temperature. The pigments coated in this manner with dyestuff are worked in the usual way. Table I summarises the lustrous pigment thereby obtained and their powder colours.

TABLE I

Interference colour of the lustrous pigment before the dyestuff coating / Dyestuff used for the coating	silvery	yellow	red	violet	blue	green
1-(2-sulpho-4-methyl-1-phenylazo)-2-naphthol-3-carboxylic acid (C-red 12)	pink	orange-pink	copper pink	bright violet red	red violet	bright red
2,4,5,7-tetra-iodofluorescein (C-red 38)	bluish pink	bluish pink	blue tinged pink	bluish pink	strong violet pink	bluish pink
1-(4-sulpho-1-naphthylazo)-2-naphthol-3,6-di-sulphonic acid (C-red 46)	soft pink	bright pink lilac	pink lilac	pink lilac	soft lilac	soft lilac
1-(2-sulphonic acid-4-chloro-5-carboxylic acid-1-phenylazo)-2-hydroxynaphthalene (C-red 8)	bright flesh colour	pink cream colour	bright yellow pink	peach blossom colour	blue tinged brick red	strong flesh colour
2-(4-sulpho-2-naphthylazo)-1-naphthol-4-sulphonic acid (C-red 54)	bright pink	bright pink lilac	coppery bright red	pale pink lilac	bluish bright red	pale pink
1-(2-sulpho-4-methyl-5-chloro-1-phenylazo)-2-hydroxynaphthalene-3-carboxylic acid (C-red 13)	bright red	bright red	bright red	violet tinged bright red	strong red violet	pink bright red
quinophthalene-disulphonic acid (C-yellow 11)	bright yellow	bright yellow	reddish bright yellow	red yellow	strong yellow	strong yellow
diethyl-di-sulphobenzyl-di-4-amino-2-chloro-di-2-methyl-fuchsonimonium (C-green 3)	pale green	pale yellow green	pale yellow green	bright green	blue green	green

TABLE I (continued)

Interference colour of the lustrous pigment before the dyestuff coating / Dyestuff used for the coating	silvery	yellow	red	violet	blue	green
1,4-di-(4'-methyl-2'-sulphophenyl-amino)-anthraquinone (C-green 11)	blue green	dark blue green	dark blue green	grey green	violet tinged blue green	green
chlorophyll (C-green 8)	blue green	blue green	dark blue green	grey green	strong blue green	blue green
indigo-di-sulphonic acid (C-blue 19)	bright blue	green tinged bright blue	red tinged bright blue	violet tinged bright blue	violet green bright blue	bright green
4'-(N-ethyl-N-*m*-sulphobenzyl-amino)-4''-(N-di-methyl-amino)-N-ethyl-N-*m*-sulpho-benzylfuchsonimonium (C-violet 10)	blue lilac	violet tinged bright blue	violet blue	strong violet blue	violet tinged dark blue	dark blue
4'-(4''-sulpho-1''-phenylazo)-7'-sulpho-1'-naphthylazo)-1-hydroxy-8-acetylamino-naphthalene-3,5-disulphonic acid (C-black 6)	bluish pigeon grey	gold shimmering violet grey	violet	violet	lilac blue	green blue
2-(4'-(4'' -sulpho-1''-phenylazo)-7'-sulpho-1'-naphthyl-azo)-1-hydroxy-7-aminonaphthalene-3,6-disulphonic acid (C-black 7)	grey	grey green	reddish grey	grey violet	dark blue	grey green

Example 8.

Analogously to Example 7, two commercially available lustrous pigments which, besides mica and titanium dioxide, also contain ferric oxide and display a strong golden powder colour, are coated with dyestuff. Both pigments display a strong yellow interference colour.

Product 1 consists of titanium dioxide-coated mica flakes with a mica content of 51.1% by weight and a titanium dioxide content of 44.4% by weight, which are coated on their surface with 4.5% by weight ferric oxide.

Product 2 consists of 56% by weight mica flakes, which are coated with a mixture of 42% by weight titanium dioxide and 2% by weight ferric oxide.

Both pigments are coated with aluminium hydroxide in the manner described in Example 7 and coloured with various dyestuffs. The following Table II gives a summary of the lustrous pigments thereby obtained and of their powder colours.

TABLE II

dyestuff	Product 1	Product 2
1-(2-sulpho-4-methyl-1-phenylazo)-2-naphthol-3-carboxylic acid (C-red 12)	deep gold orange	pink-tinged red gold
2,4,5,7-tetraiodofluorescein (C-red 38)	dark gold orange	gold pink
1-(4-sulpho-1-naphthylazo)-2-naphthol-3,6-disulphonic acid (C-red 46)	gold ochre	brown pink
1-(2-sulphonic acid-4-chloro-5-carboxylic acid-1-phenylazo)-2-hydroxynaphthalene (C-red 8)	ochre	gold brown
2-(4-sulpho-1-naphthylazo)-1-naphthol-4-sulphonic acid (C-red 54)	gold ochre	brownish pink
1-(2-sulpho-4-methyl-5-chloro-1-phenylazo)-2-hydroxynaphthalene-3-carboxylic acid (C-red 13)	gold ochre	brownish pink
diethyl-disulphobenzyl-di-4-amino-2-chloro-di-2-methyl-fuchsonimonium (C-green 3)	greenish gold	greenish yellow
1,4-di-(4'-methyl-2'-sulpho-phenylamino)-anthraquinone (C-green 11)	olive green	olive green
chlorophyll copper complex (C-green 8)	olive green	olive green
indigo-disulphonic acid (C-blue 19)	olive green	bright olive green
4'-(N-ethyl-N-*m*-sulphobenzyl-amino)-4''-(N-dimethylamino)-N-ethyl-N-*m*-sulphobenzyl-fuch-sonimonium (C-violet 10)	deep black violet	black violet
(4'-(4''-sulpho-1''-phenylazo)-7'-sulpho-1'-naphthylazo)-1-hydroxy-8-acetylamino-naphthalene-3,5-disulphonic acid (C-black 6)	bronze coloured	gold shimmering violet grey
2-(4'-(4''-sulpho-1''-phenylazo)-7'-sulpho-1'-naphthylazo)-1-hydroxy-7-aminonaphthalene-3,6-disulphonic acid (C-black 7)	brass coloured	yellow
quinaphthalone-disulphonic acid (C-yellow 11)	ochre	bright ochre

WHAT WE CLAIM IS:—

1. A coloured lustrous pigment based on mica flakes coated on both sides with an adherent coating of a metal oxide, wherein colouring is provided by an aluminium colour lake fixed, with the help of an aluminium hydroxide layer which has previously been precipitated on the metal oxide-coated mica flakes, as a water-insoluble compound on the surface of the pigment particles.

2. A pigment according to claim 1, wherein the aluminium colour lake is present in an amount of 0.001 to 5% by weight, referred to the total coloured pigment.

3. A pigment according to claim 1 or 2, wherein the mica flakes are coated with titanium dioxide and/or zirconium dioxide.

4. A pigment according to any of the preceding claims, wherein the aluminium hydroxide layer has a thickness of from 1 to 100 nm.

5. A pigment according to any of the preceding claims, wherein the colour lake is a madder lake.

6. A pigment according to any of the preceding claims, wherein the colour lake is obtained from a diazotised amine.

7. Coloured lustrous pigments according to claim 1, substantially as hereinbefore described and exemplified.

8. Process for the production of coloured lustrous pigments based on mica flakes coated on both sides with an adherent coating of a metal oxide, wherein a lustrous metal oxide-coated mica flake pigment with an aluminium hydroxide layer precipitated thereon is reacted with an aqueous solution of a hydroxyl group-containing compound which, directly or with the intermediate formation of a sparingly water-soluble precipitate with aluminium ions and subsequent reaction thereof with a diazotised amine, forms a water-insoluble aluminium colour lake.

9. Process according to claim 8, wherein the hydroxyl group-containing compound is an organic dyestuff which forms a sparingly water-soluble simple or complex salt with aluminium ions.

10. Process according to claim 8, wherein the hydroxyl group-containing compound is a chelate former which forms a sparingly water-soluble precipitate with aluminium ions, this precipitate being subsequently converted into a water-insoluble aluminium colour lake by a conventional coupling reaction with a diazotised amine.

11. Process according to claim 8 for the production of coloured lustrous pigments, substantially as hereinbefore described and exemplified.

12. Coloured lustrous pigments, whenever produced by the process according to any of claims 8 to 11.

13. Cosmetics, whenever containing at least one pigment according to any of claims 1 to 7 and 12.

14. Lacquers, whenever containing at least one pigment according to any of claims 1 to 7 and 12.

15. Synthetic resins, whenever containing at least one pigment according to any of claims 1 to 7 and 12.

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